Dipolar Interactions and Origin of Spin Ice in Ising Pyrochlore Magnets

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Recent experiments suggest that the Ising pyrochlore magnets $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ display qualitative properties of the spin ice model proposed by Harris *et al.* Phys. Rev. Lett. **79**, 2554 (1997). We discuss the dipolar energy scale present in both these materials and consider how they can display spin ice behavior *despite* the presence of long range interactions. Specifically, we present numerical simulations and a mean field analysis of pyrochlore Ising systems in the presence of nearest neighbor exchange and long range dipolar interactions. We find that two possible phases can occur, a long range ordered antiferromagnetic one and the other dominated by spin ice features. Our quantitative theory is in very good agreement with experimental data on both $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. We suggest that the nearest neighbor exchange in $Dy_2Ti_2O_7$ is *antiferromagnetic* and that spin ice behavior is induced by long range dipolar interactions.

An exciting development has occurred in the last two years with the discovery of an apparent analogy between the low temperature physics of the geometrically frustrated Ising pyrochlore compounds $Ho_2Ti_2O_7$ [1] and $Dy_2Ti_2O_7$ [2] (so called 'spin ice' materials), and proton ordering in real ice [3]. The magnetic cations Ho^{3+} and Dy^{3+} of these particular materials reside on the pyrochlore lattice of corner sharing tetrahedra. Single-ion effects conspire to make their magnetic moments almost ideally Ising-like, but with their own set of local axes. In particular, each moment has its local Ising axis along the line connecting its site to the middle of a tetrahedron to which it belongs (see inset of Fig. 1).

In a simple model of nearest neighbor ferromagnetic (FM) interactions, such a system has the same 'ice rules' for the construction of its ground state as those for the ground state of real ice [3,4]. In both cases, these rules predict a macroscopically degenerate ground state, a feature that a number of geometrically frustrated systems possess [5–8].

In $Ho_2Ti_2O_7$, μSR data indicates a lack of ordering down to $\sim$ 50 mK despite a Curie-Weiss temperature $\theta_{\rm cw} \sim 1.9$ K, while single crystal neutron scattering data suggests the development of short-range FM correlations, but the absence of ordering down to at least 0.35 K [1]. $Ho_2Ti_2O_7$ also displays field dependent behavior consistent with a spin ice picture [9]. Quite dramatically, thermodynamic measurements on $Dy_2Ti_2O_7$ [2] show a lack of any ordering feature in the specific heat data, with the measured ground state entropy within 5% of Pauling's prediction for the entropy of ice [3].

However, both spin ice materials contain further interactions additional to the nearest neighbor exchange. Often, rare earth cations can have appreciable magnetic moments and, consequently, magnetic dipole-dipole interactions of the same order as, if not larger than the exchange coupling, can occur. Furthermore, it has been suggested that the nearest neighbor exchange interaction in $Ho_2Ti_2O_7$ is actually *antiferromagnetic* (AF) [10], which by itself should cause a phase transition to a long range ordered ground state. Thus, *how* these systems actually display spin ice-like behavior is most puzzling. For example, one might naively expect that the long-range and anisotropic spin-space nature of the dipolar interactions would introduce so many constraints that a large degree of the degeneracy present in the simple nearest-neighbor ferromagnetic spin-ice model [1,4] would be removed, and induce long-range order. It is this issue that we wish to address in this paper.

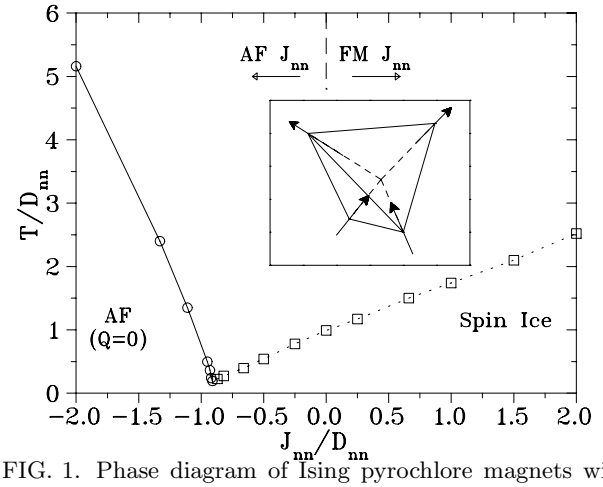

FIG. 1. Phase diagram of Ising pyrochlore magnets with nearest neighbor exchange and long range dipolar interactions. $D_{\rm nn}$ and $J_{\rm nn}$ are the Ising parameters for the nearest neighbor dipolar and exchange energies respectively (see text). *Inset:* An ice rule configuration of a tetrahedron. The four local $\langle 111 \rangle$ Ising axes meet in the middle of the tetrahedron [4].

A previous attempt to consider dipolar effects in Ising pyrochlores was made by Siddharthan *et al.* [10]. In that work, the dipole-dipole interaction was truncated beyond five nearest neighbor distances, and a sharp transition between paramagnetism and a partially ordered phase (where rapid freezing occurs) was observed for interac-

tion parameters believed appropriate for $Ho_2Ti_2O_7$ [10]. However, we argue that the truncation of dipole-dipole interactions can be misleading, and may introduce spurious features in various thermodynamic properties. For example, we find that the sharp feature observed in the specific heat for truncation beyond five nearest neighbor distances [10] is softened and rounded for truncation beyond the tenth nearest neighbor shell, and the observed dynamical freezing is pushed to lower temperatures. As we show below, in the limit of infinite range dipoles, the interaction parameters of Siddharthan *et al.* [10] yield spin ice.

In this work, we consider the interplay between nearest neighbor exchange and dipolar interactions by taking into account the long range (out to infinity) nature of the dipolar interactions through the use of Ewald summation techniques [11,12]. Our Monte Carlo simulations and mean field results show that dipolar forces are remarkably adept at producing spin ice physics over a large region of parameter space.

Some of our main conclusions are shown in Fig. 1. For Ising pyrochlores, the dipole-dipole interaction at nearest neighbor is FM, and therefore favors frustration. Beyond nearest neighbor, the dipole-dipole interactions can be either FM or AF, or interestingly, even multiply valued [13], depending on the neighbor distance. Defining the nearest neighbor dipole-dipole interaction as $D_{\rm nn}$ and the nearest neighbor exchange as $J_{\rm nn}$, our Monte Carlo results indicate that spin ice behavior persists in the presence of AF exchange up to $J_{\rm nn}/D_{\rm nn} \sim -0.91$. For $J_{\rm nn}/D_{\rm nn} < -0.91$ we find a second order phase transition to the globally doubly degenerate $\mathbf{Q} = 0$ phase of the nearest neighbor AF exchange-only model [15], where all spins either point in, or all out of a given tetrahedron.

Our Hamiltonian describing the Ising pyrochlore magnets is as follows,

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j} + D r_{\rm nn}^3 \sum_{\langle ij \rangle} \frac{\mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{z_j} \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5} , \quad (1)$$

where the spin vector $\mathbf{S}_i^{z_i}$ labels the Ising moment of magnitude $|S| = 1$ at lattice site i and *local* Ising axis z_i. Because the local Ising axes belong to the set of $\langle 111 \rangle$ vectors, the nearest neighbor exchange energy between two spins i and j is $J_{\rm nn} \equiv J/3$. The dipole-dipole interaction at nearest neighbor is $D_{\rm nn} \equiv 5D/3$ where D is the usual estimate of the dipole energy scale, $D = (\mu_0/4\pi) g^2 \mu^2 / r_{\rm nn}^3$. For both $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, $D_{\rm nn} \sim 2.35$ K.

It is well known in the field of electrostatic interactions that the dipole-dipole interaction is difficult to handle due to its $1/r^3$ nature. In general, a lattice summation of dipole-dipole interactions is conditionally convergent, and must be considered with care. In order to include the important long range nature of the dipole-dipole interaction, we have implemented the well known Ewald method within our simulation technique, in order to derive an *effective* [14] dipole-dipole interaction between spins within our simulation cell [12]. Unlike in dipolar fluid simulations, our lattice spins allow the effective interactions between all moments to be calculated only once, after which a numerical simulation can proceed as normal.

A standard Metropolis algorithm was used in our Monte Carlo simulations. We used a conventional cubic cell for the pyrochlore lattice, which contains 16 spins. In general, we found it sufficient to simulate up to $4 \times 4 \times 4$ cubic cells (*ie.* L=4, and 1024 spins) with up to $\sim 10^6$ Monte Carlo steps per spin when necessary. Thermodynamic data were collected by starting the simulations at high temperatures and cooling very slowly.

Referring to Fig. 1, the characterization of a system as having spin ice behavior was carried out by determining the entropy, via numerical integration of the specific heat divided by temperature data. Pauling's argument for the entropy of ice yields $R[\ln 2 - (1/2)\ln(3/2)]$ or 4.07 J mol^{-1} K^{-1} [2,3]. We find for $J_{\rm nn}/D_{\rm nn} = -0.91$, (our spin ice data point closest to the phase boundary in Fig. 1), this value for the entropy to within 3%, using a system size $L = 4$.

Our thermodynamic data indicates that when the nearest neighbor exchange is AF and large compared to the dipolar interactions, the system undergoes a second order phase transition to an all in or all out $\mathbf{Q} = 0$ ground state as alluded to earlier. This AF phase persists slightly beyond the point where the nearest neighbor dipolar interaction (FM) is stronger than nearest neighbor AF exchange.

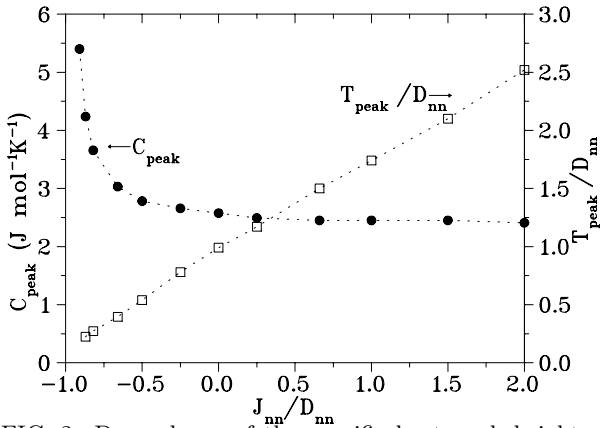

FIG. 2. Dependence of the specific heat peak height and temperature location on exchange and dipole-dipole interaction parameters.

In the spin ice regime, our specific heat data has a number of interesting features which help shed light on the effect of long range dipole-dipole interactions. In general,

each data set shows qualitatively the same broad peak as observed in the nearest neighbor FM exchange model, and vanishes at high and low temperatures [9,10]. We detect very little system size dependence upon comparison of data from $L = 2, 3, 4$ simulation sizes. In particular, there is no noticeable size dependence of the specific heat maximum, nor its position. As the AF/spin ice phase boundary is approached from the spin ice side, the specific heat peak begins to narrow and more importantly, both the peak height and peak position begin to vary. As we discuss below, this has important ramifications for the interpretation of experimental data.

In Fig. 2 we plot the dependence of the specific heat peak height ($C_{\rm peak}$) and the temperature at which it occurs ($T_{\rm peak}$) on the ratio of the nearest neighbor exchange and dipole-dipole energies, $J_{\rm nn}/D_{\rm nn}$. Note that in the regime of large nearest neighbor FM coupling, the peak height plateaus to the value one observes in the nearest neighbor FM exchange-only model.

Indeed our data suggests that when the exchange becomes FM, the nearest neighbor effective bond energy is large enough to dominate the excitations of the system. This can be more dramatically seen in Fig. 3, where we have rescaled the specific heat curves for a number of interaction parameter values in terms of the effective nearest neighbor interaction $J_{\rm eff} \equiv J_{\rm nn} + D_{\rm nn}$ in the regime $J_{\rm nn}/D_{\rm nn} > 0$.

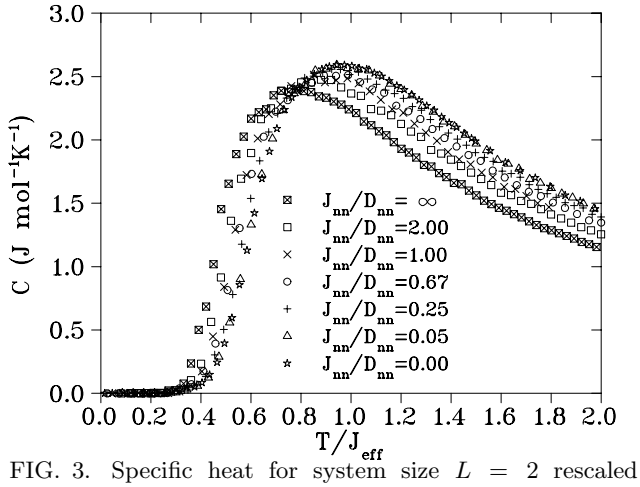

FIG. 3. Specific heat for system size $L = 2$ rescaled into units of the effective nearest neighbor interaction $J_{\rm eff}$. $J_{\rm nn}/D_{\rm nn} = 0$ corresponds to purely dipolar interactions while $J_{\rm nn}/D_{\rm nn} = \infty$ corresponds to nearest neighbor FM exchange only.

This figure shows that in terms of an effective energy scale, the medium to long range effects of the dipolar interactions are 'screened' by the system, and one recovers qualitatively the short range physics of the nearest neighbor spin ice model. Remarkably, inclusion of long range dipolar interactions appears to have the effect of *removing* a tendency towards ordering which can come from a short range truncation of the dipole-dipole interaction.

As the nearest neighbor exchange interaction becomes AF, we find that the approximate 'collapse' onto a single energy scale becomes less accurate, with features in the specific heat becoming dependent on $J_{\rm nn}/D_{\rm nn}$ in a more complicated manner. It is within this regime that we believe that both $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ exist.

Since $D_{\rm nn}$ is a quantity which can be calculated once the crystal field structure of the magnetic ion is known, the nearest neighbor exchange $J_{\rm nn}$ is the only adjustable parameter in our theory. Fig. 2 enables us to test in two independent ways the usefulness of our approach to the long range dipole problem in spin ice materials.

If we consider $Dy_2Ti_2O_7$ for example, specific heat measurements by Ramirez *et al.* [2] indicate a peak height, $C^{\rm Dy}_{\rm peak}$ of ~ 2.72 J mol^{-1}K^{-1}. Given that $D_{\rm nn} \approx 2.35$ K for this material, the left hand plot of Fig. 2 indicates a nearest neighbor exchange coupling $J_{\rm nn} \sim -1.2$ K. The same experimental specific heat data shows that this peak occurs at a temperature of $T_{\rm peak^{Dy}} \sim 1.25$ K. Using the plot of $T_{\rm peak}$ in Fig. 2, we independently arrive at approximately the same conclusion for the value of the nearest neighbor exchange. Thus, we predict that AF exchange is present in $Dy_2Ti_2O_7$ with $J_{\rm nn} \sim -1.2$ K. If there was no AF exchange present in this system, our results in Fig. 1 imply that there would be a peak in the specific heat at a temperature of at least ~ 2.3 K, which is not observed experimentally [2]. Our best fit for the specific heat data of $Dy_2Ti_2O_7$ by Ramirez *et al.* [2] is shown in Fig. 4, where we find good agreement between theory and experiment for $J_{\rm nn} = -1.24$ K.

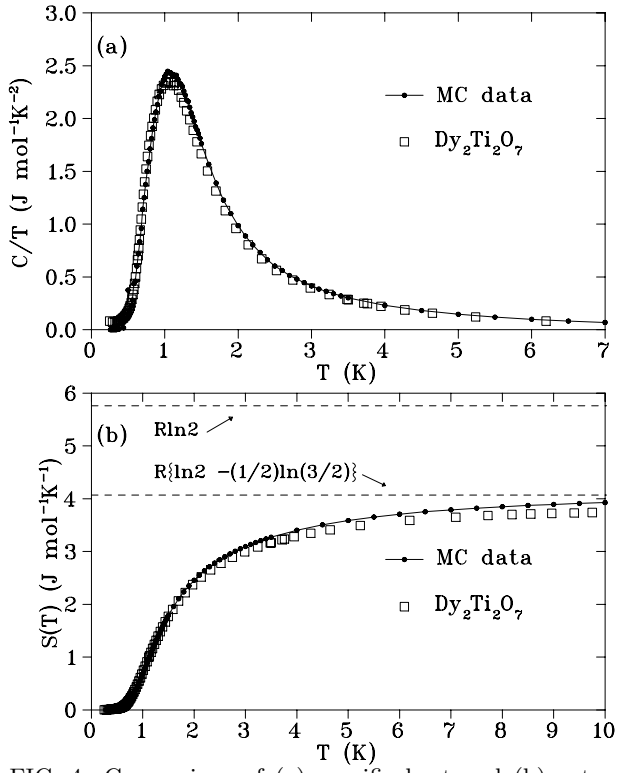

FIG. 4. Comparison of (a) specific heat and (b) entropy data between $Dy_2Ti_2O_7$ [2] and Monte Carlo simulation with $J_{\rm nn} = -1.24$ K, $D_{\rm nn} = 2.35$ K and system size L=4.

Specific heat measurements on a powdered sample of $Dy_2Ti_2O_7$ in a magnetic field were also reported in Ref. [2]. Three field independent peaks were observed at low temperature. For a large field in the $\langle 110 \rangle$ direction, two spins on each tetrahedron are pinned by the field, while the other two remain free, since their Ising axes are perpendicular to the applied field. Due to the dipolar interaction, there will be a coupling between the fluctuating spins on these two sub-lattices. Our preliminary simulations on small lattice sizes suggest a field independent ordering at low temperature as observed in experiment.

Considering $Ho_2Ti_2O_7$, experimental data on its thermodynamic properties is not so categorical. The specific heat data of Siddharthan *et al.* [10] indicates a feature at ~ 0.8 K, although it has been suggested that this could be due to an additional contribution in this temperature range from an anomalously large hyperfine coupling in Ho^{3+} [18]. Nevertheless, using the plot of $T_{\rm peak}$ in Fig. 2, we find substantial AF exchange coupling of the same order of magnitude as in the Dy compound. We note that Siddharthan *et al.* [10] and den Hertog *et al.* [18] find from analysis of magnetization measurements a similar order of magnitude for $J_{\rm nn}$. Furthermore, our numerical simulations within this region of parameter space indicate a Curie-Weiss temperature of ~ 2 K, in agreement with an experimental estimate by Harris *et al.* of $\theta_{\rm cw} \sim 1.9$ K [1].

$Tb_2Ti_2O_7$ is an Ising pyrochlore system of similar type to the Ho^{3+} and Dy^{3+} based materials [7,8], but the Ising anisotropy is reduced to much lower temperature due to narrowly spaced crystal field levels [8]. While this makes the interpretation of experimental data more difficult, initial estimates of the nearest neighbor exchange and dipole moment [8] yield $J_{\rm nn}/D_{\rm nn} \sim -1$, placing this system very close to the phase boundary of Fig. 1. Indeed, μSR measurements suggest that $Tb_2Ti_2O_7$ fails to order down to 70 mK [7] and thus it would appear that a spin ice picture for this material cannot be *a priori* ruled out.

While we believe our approach yields a reasonably successful quantitative theory of spin ice behavior in Ising pyrochlores, there still remains the question of why long range dipolar interactions do not appear to lift the macroscopic degeneracy associated with the ice rules, and select an ordered state.

Mean-field theory provides a more quantitative basis for examining this issue. Following the approach used in Refs. [16,17], we find that the soft-modes for Ising pyrochlore systems described by Eq. 1 consist of two very weakly dispersive branches (less than 1% dispersion) over the whole Brillouin zone (except at $\mathbf{Q} \equiv 0$). Such a set of quasi-dispersionless branches is very similar to the two completely dispersionless soft branches of the nearest-neighbor FM spin ice model. Consequently, both nearest-neighbor FM and dipolar spin ice behave almost identically over the whole temperature range spanning $O(w) \leq T < \infty$ where w is the bandwidth of the soft branch of dipolar spin ice. We note that this near dispersionless behavior is only recovered *asymptotically* as the long range dipoles are included out to infinity. The lifting of degeneracy at the 1% level in the apparent absence of any small parameters in the theory is at this point not completely understood. We do not believe it is due to numerical or computational error. A partial explanation may be that (111) Ising anisotropy, the $1/r^3$ long-range nature of dipolar interactions, and the specific relationship between the topology of the pyrochlore lattice and the anisotropic (spin−space) coupling of dipolar interactions, combine in a subtle manner to produce a spectrum of soft modes that *approximate* very closely the spectrum of the nearest-neighbor ferromagnetic spin ice model of Harris et al. [1]. In other words, there must be an almost exact symmetry fullfilled in this system when long-range dipolar interactions are taken into account. However, the same long-range nature of these interactions renders it difficult to construct a simple and intuitive picture of their effects, and we have not been able to identify such "almost exact" symmetry.

Also, in these systems, the absence of soft fluctuations (Ising spins) combined with the macroscopic degeneracy associated with the ice rules may be such that correlations associated with a 'true' ground state are dynamically inhibited from developing. For energetic reasons, states obeying the ice rules are favored down to low temperature, by which time such large energy barriers exist that evolution towards the true ground state is never

achieved. In simulation terms, at low temperature the Boltzmann weights for local spin flips 'towards' this state are simply too small.

In conclusion, using Ewald summation techniques we have considered the effects of long range dipole-dipole interactions on the magnetic behavior of Ising pyrochlore systems. Our results show that spin ice behavior is recovered over a large region of parameter space, and we find quantitative agreement between our approach and experimental data on spin ice materials.

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[1] M. J. Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997).
[2] A. P. Ramirez *et al.*, Nature **399**, 333 (1999).
[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), p. 301.
[4] For the particular type of Ising pyrochlores discussed here, the ice rules imply that every tetrahedron must have two spins pointing into it, and two pointing out.
[5] J. Villain, Z. Phys. B **33**, 31 (1979).
[6] R. Moessner and J. T. Chalker, Phys. Rev. Lett. **80**, 2929 (1998).
[7] J. S. Gardner *et al.* Phys. Rev. Lett. **82**, 1012 (1999).
[8] M. J. P. Gingras *et al.*, cond-mat/0001317, unpublished (1999).
[9] M. J. Harris *et al.*, Phys. Rev. Lett. **81**, 4496 (1998).
[10] R. Siddharthan *et al.*, Phys. Rev. Lett. **83**, 1854 (1999).
[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1968), p. 228.
[12] S. W. de Leeuw, J. W. Perram and E. R. Smith, Proc. R. Soc. Lond. A **373**, 27 (1980).
[13] This is due to the nature of the local Ising axes. For example, there are 12 third nearest neighbors to a spin i. Six have displacement vectors $\mathbf{r}_{ij}$ which are perpendicular to their local Ising axis, giving two values for the dipolar interaction at this neighbor distance.
[14] Physically, this corresponds to having an infinite number of replicas of the simulation cell, and using the Ewald method to sum convergently the dipolar interaction between say spins i and j (within the simulation cell) and spin j's images (outside the simulation cell). The result, is the effective Ising interaction of spin i with spin j.
[15] S. T. Bramwell and M. J. Harris, J. Phys. Condens. Matter **10**, L215-L220 (1998).
[16] J. N. Reimers, A. J. Berlinsky and A. -C. Shi, Phys. Rev. B **43**, 865 (1991).
[17] N. P. Raju *et al.* Phys. Rev. B **59**, 14489 (1999).
[18] B.C. den Hertog et al., cond-mat/9912220, unpublished (1999).